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FORMATION OF HALOGENATED ORGANICS BY CHLORINATION OF WATER SUPPLIES

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Available literature on the formation of halogenated organic compounds during the chlorination of water supplies has been reviewed critically. Types of organic compounds likely to be encountered in natural waters have been surveyed and various known or prospective reactions of dilute aqueous chlorine with these types of compounds have been discussed.

It is concluded that two principal types of chlorination reaction are expected: (1) electrophilic aromatic chlorination as in the long-known formation of chlorophenols; and (2) electrophilic chlorine addition to activated double bonds like that of enolacetone. Chloroform or other haloforms may occur as end products of exhaustive chlorination in either case. General substitution reactions of chlorine are unlikely however. So carbon tetrachloride or fully chlorinated higher hydrocarbons are not probable products of water chlorination.

Possible methods for minimizing the concentrations of halogenated organic compounds in municipal supplies have been outlined. These include pretreatment methods, such as coagulation or preozonation to reduce amounts of precursors to the halogenated compounds, and posttreatment methods, such as carbon adsorption or aeration to remove halogenated compounds after their formation.

Needed research has been described.

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ABSTRACT

Available literature on the formation of halogenated organic compounds during the chlorination of water supplies has been reviewed critically. Types of organic compounds likely to be encountered in natural waters have been surveyed and various known or prospective reactions of dilute aqueous chlorine with these types of compounds have been discussed.

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Needed research has been described.

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CONCLUSIONS

The finding of product haloforms as a result of the chlorination of relatively unpolluted surface water supplies poses a serious problem for agencies producing domestic water supplies, for chlorination is the almost universal procedure used to protect against the water-borne transmission of infectious diseases. The problem lies not so much in the production of the haloforms themselves as it does in the possibility that other, unknown, highly toxic or carcinogenic compounds may also be produced simultaneously.

A careful review and assessment of available literature relating to the formation of chlorinated organic compounds under conditions prevailing in natural waters leads to the conclusion that chlorination is not indiscriminate, and so does not lead to the formation of all sorts of chlorinated derivatives with any and all organic pollutants. Rather it proceeds by a limited number of well-defined reactions on a few specific types of organic structures.

The identifiable initial reactions are electrophilic aromatic substitution of positive chlorine and electrophilic addition of positive chlorine to appropriately activated double bonds. The former reaction, which produces malodorous chlorophenolic compounds in intermediate stages, leads ultimately to oxidative ring rupture. The latter process leads to chloroform (and other haloforms when bromide is present) as the end product.

Direct substitution reactions of aqueous chlorine leading to the formation of exhaustively chlorinated hydrocarbons are unknown and unlikely. The known mechanisms do not lead to such exhaustively chlorinated products as carbon tetrachloride or tetrachloroethylene.

Reduction in the concentration of chlorinated organic compounds in finished municipal supplies can be achieved either by pretreatment methods to remove organic precursors or by post-treatment with activated carbon.

RECOMMENDATIONS

Because this contract was limited to the review and assessment of currently available information, no experimentation was conducted to see whether the judgments that have been reached are generally sound. The reports on the formation of the haloforms have been initial findings; much additional research is needed to determine more fully conditions for the occurrence of the phenomenon, its extent and the full range of products.

First efforts should be directed to a determination of the formation of other chlorinated organics than the haloforms. Investigations to this end should include stoichiometric and dynamic considerations. Effects of chlorine dosage relative to organic matter, yields of chlorinated organic materials relative to applied chlorine and to organic content, and influence of time of reaction on the nature and yield of organic materials all need prompt study.

Second, the effects of possible pretreatment steps on the extent of production of chlorinated organic compounds should be investigated to determine which may be most useful in minimizing the problem. This study should be correlated with more fundamental ones to discover the types of materials and the structures responsible for the production of the chlorinated derivatives.

There should be no relaxation of the practice of water chlorination in the meantime. Protection of the public health depends strongly on continuation and even intensification of water chlorination. Until there is some positive indication that the formation of chlorinated organic compounds during the disinfection of water supplies has hygienic significance, there should be no attempt to make widespread modifications in water treatment. Useful modifications should be developed, however, so that they are promptly available if a need for change is shown.

Introduction

In recent months concern about the presence and production of chlorinated organic compounds in water supplies has been greatly intensified because of findings of numerous chlorinated organic compounds in drinking water derived from the lower Mississippi River [47, 152, 31] and because of the discovery by Rook (124) and later by Bellar, Lichtenberg and Kroner (10) that chloroform and other halogenated methanes are formed during the chlorination of water for disinfection. It should be noted that these findings came as a result of the development of more sensitive and refined analytical techniques and not because the occurrence or production of the compounds is a recent situation.

There are four principal ways in which chlorinated organic compounds may occur in water supplies: from non-point sources, from industrial discharges, from chlorination of sewage or industrial wastewater and by the chlorination of organic matter in the water supply. Different problems are posed with each of these sources and different solutions may be required in each instance. Accordingly, it is important that the categories be kept distinct when consideration is given to the generality or seriousness of the overall situation and when measures are being developed to deal with them.

1. Non-point Sources. Chlorinated organic compounds may be introduced into rainfall from atmospheric pollution or may be incorporated into surface runoff to find their way into streams, lakes and rivers. Although these sources have been incriminated in connection with health effects on

aquatic life, they seem not to have led to sufficiently great concentrations of known materials in drinking waters to have become a major direct problem to human health. As is recognized, problems that may arise from these sources of chlorinated organic compounds may be dealt with either by restricting dissemination of the materials in the environment or by special treatment to remove them.

The materials of importance in connection with non-point pollution are pesticides, fungicides, weed killers and other agricultural chemicals plus the polychlorinated biphenyls. The possibility that precursors of hazardous chlorinated compounds may be introduced into water supplies in this way to be converted ultimately into harmful products when the water is chlorinated must not be overlooked, but no significant instance of such an occurrence seems to have been observed until now.

The problem of chlorinated organic compounds that may be found in water supplies as a result of contamination from non-point sources does not fall within the scope of this report and will not be considered further.

2. Industrial Discharges. The major source of chlorinated organic compounds in water supplies is industrial discharge, both the intentional discharge of wastewaters from manufacturing plants and accidental spillages of chlorinated compounds that find their way eventually into water courses. The variety of chlorinated organic compounds found in the Ohio and the lower Mississippi Rivers (86, 10, 152) comes from such industrial discharges. Similarly, the 50 chlorinated organic compounds reported to have been found in Rhine water by Sondheimer (141) are considered to be almost wholly of industrial origin.

Finding of chlorinated organics in drinking waters derived from sources such as the lower Mississippi and Rhine has bearing on the question of the production of chlorinated organic compounds during water disinfection by chlorination only to the extent that the types or concentrations of chlorinated compounds are shown to have been increased following this step in water treatment.

Procedures for the alleviation of problems caused by the presence of chlorinated organic compounds from this source are, first of all, enforced regulation of industrial discharges and, secondly, supplementary treatment of the water by adsorption on activated carbon or chemical oxidation to eliminate the offensive materials. Once again, detailed discussion of this source of chlorinated organic compounds does not fall within the scope of this report. It may be noted, however, that problems arising in this way are limited to localities that use industrially polluted waters as their source of drinking water and thus are not associated universally with basic procedures of water treatment.

3. Sewage Chlorination. R.L. Jolley (83) has shown in a very important publication that the practice of chlorination of municipal wastewater effluents for the purpose of disinfection results in the formation of numerous chlorinated organic compounds, seventeen of which were identified. The yield of these chlorinated organic compounds was not great, comprising in total only about 1% of the chlorine dose.

This research has little direct bearing on questions of the formation of chlorinated organic compounds during water chlorination except that it points up the possibility of direct aqeuous chlorination of a wide range of

organic compounds, some of which may also be encountered in water supplies. The chlorination conditions for sewage effluents and for water supplies are very different, however. In the former instance there is essentially immediate complete formation of chloramine which then serves as the reactive agent; in the latter instance it is normal to have present an excess of the strongly oxidizing HOCl.

The seventeen compounds identified by Jolley all contained only a single chlorine atom. In general such minimally chlorinated compounds are much more readily degraded biochemically than are the polychlorinated materials that have been found to be so perdurent in the environment. Accordingly, it seems unlikely that any of these materials will persist in receiving waters long enough to cause major problems at downstream water treatment plants or that they will biologically accumulate in organisms to any great extent.

4. Water Chlorination. That the chlorination of water supplies produces chlorinated derivatives of organic compounds present is not a new discovery. From almost the first years of the practice of water chlorination, the formation of "chlorophenols" with their accompanying tastes and odors has been a nagging problem for operators of water treatment plants. As early as 1922, only a dozen years after the first sustained municipal chlorination in this country, Donaldson (30), wrote: "Since the early days of chlorination there has been recognized the probability of organic matter combining with chlorine and thus giving rise to disagreeable tastes."

The main concern in this and other early reports (18, 30, 36, 42, 53, 149) however, was the tastes and odors produced in the formation of these chlorinated compounds. Provided tastes and odors were controlled there was little systematic concern about other physiological effects of

chlorinated compounds in the distributed waters.

Along with the recent development of awareness of the physiological hazards associated with many chlorinated compounds such as DDT, dieldrin, polychlorinated biphenyls and vinyl chloride, there has come to be a general opprobrium attached to any chlorinated organic compound. Accordingly, the reports of the production of halogenated methanes in the chlorination even of unpolluted water supplies have had a strong impact, partly because of the resulting distribution of the halogenated methanes themselves and partly because of the possibility that other more hazardous and as yet undetected halogenated compounds are also being produced. Prospective hazards from either of these sources call into question the whole process of water chlorination by which the freedom of our drinking water from microbial contamination is assured.

Accordingly, it is essential that the total significance of these reports be assessed as promptly as possible in order that the proper integrity of our drinking water supplies be maintained to the highest degree. The total range of chlorinated compounds formed during water chlorination and the conditions of their formation are not presently known. In the absence of firm experimental data it is necessary to estimate probable products and conditions of formation from what is known about the general chemical behavior of aqueous chlorine and the nature of the organic chemical compounds that may be found in natural waters. Although such an estimation can only be a temporary stopgap pending the acquisition of firm experimental evidence, it may serve to indicate the need for emergency measures during the interim period and may also show the direction in which ultimate solutions should be sought.

The subsequent sections of this report will deal first with the types of reactions of aqeuous chlorine with various classes of organic compounds. Then the types of organic compounds either known to be present or likely to occur in natural waters will be described and their known or probable interactions with available chlorine during water chlorination will be surveyed. After a detailed evaluation of the findings of Rook and Bellar, Lichtenberg and Kroner, the prospective health hazards associated with water chlorination will be considered and assessed to the extent that our present knowledge permits.

Next, possible modifications in treatment to minimize formation of chlorinated organic compounds during the process of water chlorination will be described. Finally recommendations will be made for research that needs to be carried out to establish experimentally the significance and hazards of the formation of chlorinated organic compounds in the disinfection of water supplies by chlorination.

Aqueous Chlorination Reactions

The central and most significant fact about aqueous chlorination in the range of concentrations employed in water treatment is that elemental chlorine, Cl_2, is not involved. When chlorine is dispersed in water at pH greater than five in concentrations up to 100 mg per liter or about 10^{-3} molar, the Cl_2 is hydrolyzed essentially instantaneously and completely (better than 99.99%) to HOCl and OCl^- (83, 91) in accordance with the equations

$$Cl_2 + HCO_3^- \rightarrow HOCl + Cl^- + CO_2 \qquad (1)$$

$$HOCl \rightleftarrows H^+ + OCl^- \qquad (2)$$

So, it is necessary to consider the reactions of hypochlorite rather than those of Cl_2 in describing the potential interactions of dilute aqeuous chlorine with organic compounds.

There are four principal types of reaction of hypochlorite with organic matter in dilute aqueous solution that need to be considered. These are:

(1) Addition to olefinic bonds as illustrated by the type reaction

$$R_1 - \overset{H}{\underset{|}{C}} = \overset{H}{\underset{|}{C}} - R_2 + HOCl \rightarrow R_1 - \overset{H}{\underset{OH}{\overset{|}{\underset{|}{C}}}} - \overset{H}{\underset{Cl}{\overset{|}{\underset{|}{C}}}} - R_2 \qquad (3)$$

(2) Activated ionic substitution as illustrated by the type reactions

$$C_6H_5OH + HOCl \rightarrow C_6H_4ClOH + H_2O \qquad (4)$$

$$CH_3\overset{O}{\overset{\|}{C}} - CH_3 + HOCl \rightarrow CH_2Cl - \overset{O}{\overset{\|}{C}} - CH_3 + H_2O \qquad (5)$$

In each of these instances formation of the chlorinated derivative is preceded by an ionization and formation of a carbanion to which the positive chlorine of HOCl becomes attached (96, 155).

(3) Oxidation, with reduction of the hypochlorite chlorine to chloride as illustrated by the aldehydic oxidation

$$R - CHO + HOCl \rightarrow RCOOH + H^+ + Cl^- \qquad (6)$$

(4) Substitution of chlorine for hydrogen on a nitrogen atom as shown by the typical reaction

$$R_1 - \underset{H}{N} - R_2 + HOCl \rightarrow R_1 - \underset{Cl}{N} - R_2 + H_2O \qquad (7)$$

Any of these reactions may be succeeded by additional reactions of the same type or of the other types; there may also be, following elimination, hydrolysis or migration reactions, depending on the structure or reactivity of the initial products.

One type of reaction that is <u>not</u> to be expected is simple aliphatic substitution as illustrated by the equation

$$CH_3 - CH_3 + HOCl \rightarrow CH_3 - CH_2Cl + H_2O \qquad (8)$$

This type of reaction is nearly always a radical chain reaction, requiring light, much thermal energy or an initiator and proceeding best in non-ionizing environments.

The first three types of reaction convert the chlorine either to chloride ion or to a covalently bound state in which the chlorine no longer acts as an oxidizing agent toward iodide or other readily oxidized materials. These reactions, therefore, represent the exertion of "chlorine demand",

the conversion of active or available chlorine to a non-oxidizing form. Chlorine demand always accompanies the formation of C-chlorinated organic compounds; the chlorine demands of water supplies thus reflect in some measure the potential for formation of chlorinated compounds during disinfection.

The yield of chlorinated compounds will vary of course with the nature of the organic material. Jolley (83) for example, found that in the chlorination of sewage effluent only about 1% of the applied chlorine ended up as chlorinated product.

In contrast the chlorine that reacts to substitute on nitrogen does not lose its oxidizing capacity, although the vigor and potency of the oxidizing action may be reduced. Subsequent reactions of the N-chlorinated compounds, or chloramines, may also produce C-chlorinated compounds; so they, too, are part of the active residual chlorine.

A. Reactions with Nitrogenous Substances. The last type of reaction, that to form N-chlorinated compounds, will be discussed in detail first. Reaction in accordance with Equation (7) occurs quite generally with all sorts of nitrogenous compounds - amines, amides, amino acids, proteins and heterocyclic compounds - and often proceeds rapidly, especially with the more basic nitrogen atoms. The reaction with ammonia, for example, requires only about a minute at the milligram per liter (10^{-4}M) level at neutral pH.

When the nitrogenous reactant is a simple primary or secondary amine, the N-chlorinated product is normally quite stable in dilute aqueous solution and may persist for several days unless the chlorine is converted to chloride by reaction with reducing materials or unless chlorination on carbon like

that with hypochlorite occurs. These latter types of reactions are presumably much slower than the corresponding hypochlorite reactions, but cannot be ruled out completely.

When the nitrogenous material is a tertiary amine, so that no H atom on N is available for replacement by Cl, an interesting oxidative cleavage occurs with production of an N-chloro secondary amine and an aldehyde (24, 35) which may subsequently be oxidized by excess of hypochlorous acid. A typical reaction sequence is

$$R_1R_2N - CH_2 - R_3 + 2\ HOCl \rightarrow R_1R_2\ NCl + R_3CHO + H_2O + H^+ + Cl^- \quad (9)$$

$$R_3CHO + HOCl \rightarrow R_3COOH + H^+ + Cl^-$$

α-Amino acids upon chlorination give first N-chlor derivations, but then, in general, oxidative deamination occurs giving an α-keto acid and ammonia chloramine. With an excess of hypochlorous acid the keto acid, depending on its structure, may be additionally oxidized and the nitrogen will go through the breakpoint process. (28, 46, 78, 89). With alanine, for example, the initial reactions are

$$CH_3 - \underset{\underset{NH_2}{|}}{\overset{\overset{H}{|}}{C}} - COOH + HOCl \rightarrow CH_3\underset{\underset{NHCl}{|}}{\overset{\overset{H}{|}}{C}} - COOH + H_2O \quad (10)$$

$$CH_3 - \underset{\underset{NHCl}{|}}{\overset{\overset{H}{|}}{C}} - COOH + HOCl \rightarrow CH_3 - \underset{\underset{O}{\|}}{C} - COOH + NH_2Cl + H^+ + Cl^- \quad (11)$$

The chlorination of glycine is a special case. In addition to the oxidative deamination to CHOCOOH and NH_2Cl, decarboxylation occurs yielding finally CNCl and CO_2 as carbonaceous products (28, 90, 113, 166). No evidence for formation of other C-chlorinated organic compounds as a result of these reactions has been found, however.

Heterocyclic ring compounds containing basic nitrogens, such as pyrimidines, purines, pyrroles and indoles exhibit complex reactions with aqueous chlorine. Pyrimidines, especially those with a 2- or 4- amino group, react readily with aqueous chlorine, not only to form chloramines, but also to give C-chlorinated derivatives, particularly the 5-chloro compounds. (117, 120). Purines appear to be simultaneously oxidized and chlorinated (69, 83). Chlorination by mechanisms similar to aromatic substitution seems to occur with pyrroles and indoles (83, 106). None of these reactions has been investigated at the concentrations and conditions of water chlorination, but clearly a possibility exists that aqueous chlorination of these types of compounds, to the extent that they exist in raw water supplies, is a source of chlorinated organic compounds.

Amides and imides react less rapidly with hypochlorite than amines, so much so that some investigators have found no reaction at the concentrations used in water treatment (126, 129,115). Rearrangements of these N-chloroamides may occur by a mechanism akin to the Hofmann reaction to give amine plus CO_2, with subsequent chlorination of the amine in the presence of excess hypochlorite. Rearrangements of aromatic N-chloroamides or N-chloranilides may give rise to chlorine substitution on aromatic carbon. Presumably subsequent reactions of these chlorinated aromatic rings will resemble that of the chlorinated phenols.

In summary, it appears that although there is extensive reaction of hypochlorite with nitrogenous substances, there is little evidence for formation of stable C-chlorinated materials as a result of N-chlorination.

B. Oxidation Reactions. Oxidation by aqeuous hypochlorite, like chlorine substitution, does not occur readily with simple saturated aliphatic hydrocarbon chains. Some point of attack is needed where some sort of substitution or unsaturation is already present. Alcoholic, aldehydic, carbohydrate types of materials, those for which hydrolysis to hydroxylated substances can take place and compounds with sulfhydryl groups or other reduced sulfur linkages are all classes of compounds subject to oxidation by aqueous hypochlorite. Since no substitution of chlorine into the organic compounds occurs in this type of oxidation, there is no need to explore the great number and variety of such reactions in detail. Because oxidation reactions of aqueous hypochlorite are common and extensive, however, it is highly probable that most of the chlorine demand of natural waters results in production of chloride ions rather than chlorinated organic compounds.

C. Addition to Olefinic Bonds. The standard reaction of hypochlorous acid with olefinic double bonds is to produce chlorohydrins as shown in Equation 3 (25, 26, 83). The CHOH group in this type of addition product is then subject to additional oxidation and possible rupture of the carbon chain at this linkage. In some instances a dichloro compound may be produced even though HOCl is the responsible agent, for the first step in the accepted mechanism is an opening of the double bond with addition of Cl^+. The other end of the double bond may then react with OH^- or Cl^- or possibly other anions in the aqueous solution. So far as it is known there has been no investigation of possible ultimate products in the presence of excess HOCl.

D. Reactions with Aromatic Compounds. The typical first reaction of HOCl with aromatic compounds is a substitution of Cl for H on the aromatic ring, presumably by way of an additive intermediate. When the substrate is the aromatic hydrocarbon itself, however, a strong acid must also be present to give H_2OCl^+ or Cl^+ as the actual chlorinating agent. When the aromatic ring is activated by an appropriate substituted group, the OH group being a prime example, then substitution of Cl on the aromatic rings will proceed readily even in neutral aqueous solution (91, 20, 96).

The traditional chlorination reaction of phenol proceeds readily by way of o-chlorophenol and p-chlorophenol formation through 2,4-dichlorophenol and 2,6-dichlorophenol to 2,4,6-trichlorophenol (19, 91,83). At this point, however, dilute aqueous chlorination becomes much slower or more difficult, so that oxidative rupture of the benzene ring becomes dominant, yielding at first two-carbon residues and eventually CO_2, H_2O and Cl^- (74, 91,78). A preferred pathway of oxidation appears to be through hydrolytic oxidation and elimination of Cl^- from the 2 or 6 position to give o-benzoquinone with subsequent ring rupture at the other positions.

Homologs and analogs of phenol, including cresols, hydroquinones, anisole and 2-methoxy-4-methylphenol react similarly (8, 52,142). In the last instance the two ring-carbon residues, oxalic acid and methylfumaric acid were observed as products after ring rupture.

Aromatic aldehydes and acids, including benzoic acid, salicyclic acid, p-hydroxybenzoic acid, anisic acid, vanillic acid, vanillin, 2,4-dihydroxybenzaldehyde, phenoxy-acetic acid and phthalic acid may also be chlorinated in aqueous solution (68, 58). Reactions have not been

studied with excess hypochlorite to determine whether ring rupture also occurs with these compounds; it seems likely by analogy that it would also occur in these instances, however.

Heterocyclic aromatic rings exhibit great variations in reactivity toward chlorine substitution. Pyridine, for example, is much less reactive than benzene and so does not chlorinate readily in aqueous solution. Pyrrole, on the other hand, is activated, and so may be expected to give chlorinated derivatives as phenol does (106, 46). Friend found that the amino acid, proline, exhibited rapid chlorine demand after N-chlorination, perhaps indicating a rupture of the 5-membered heterocyclic ring.

E. The Haloform Reaction. An aqueous chlorination reaction of particular interest in connection with the treatment of water supplies is the haloform reaction, which occurs generally in alkaline aqueous solution with organic compounds containing the acetyl group $CH_3-\overset{O}{\overset{\|}{C}}-$ or with structures such as CH_3CHOH- that may be oxidized to the acetyl group. The three hydrogens of the methyl group are successively replaced by chlorine or other halogen and then the carbon bond to the carbonyl group is split giving rise to a haloform and a carboxylic acid. The overall reactions may be written

$$CH_3COR + 3HOCl \rightarrow CCl_3COR + 3H_2O \qquad (11)$$

$$CCl_3COR + H_2O \rightarrow CHCl_3 + RCOOH \qquad (12)$$

The accepted mechanism for the reaction is an initial dissociation of H^+ to yield a carbanion which then adds positive halogen. Subsequent dissociation and addition of positive halogen continue at the same carbon until it is fully halogenated. Then nucleophilic base attack displaces the

CCl_3^- group, which combines with H^+ to give chloroform ( ).

The complete sequence of mechanistic reactions is

$$RCOCH_3 \rightarrow R\overset{O^-}{C} = CH_2 + H^+ \quad (13)$$

$$R\overset{O^-}{C} = CH_2 + HOCl \rightarrow RCOCH_2Cl + OH^- \quad (14)$$

$$RCOCH_2Cl \rightarrow R\overset{O^-}{C} = CHCl + H^+ \quad (15)$$

$$R\overset{O^-}{C} = CHCl + HOCl \rightarrow R\overset{O}{C}CHCl_2 + OH^- \quad (16)$$

$$RCOCHCl_2 \rightarrow R\overset{O^-}{C} = CCl_2 + H^+ \quad (17)$$

$$R\overset{O^-}{C} = CCl_2 + HOCl \rightarrow RCOCCl_3 + OH^- \quad (18)$$

$$RCOCl_3 + OH^- \rightarrow RCOOH + CCl_3^- \quad (19)$$

$$CCl_3^- + H^+ \rightarrow CHCl_3 \quad (20)$$

The slowest step in this sequence of reactions is reaction 13, so that once the beginning reaction is initiated, the ultimate formation of chloroform is reached at the same rate as that at which the first reaction occurs. It, therefore, makes no difference what the halogenating agent is in reactions 14, 16, and 18; the reaction proceeds at the same overall rate as the initial rate-determining step, reaction 13. This has been observed experimentally.

It may be noted, however, that when mixed halogenating agents, say HOCl and HOBr, are present, then the relative amounts of $RCOCH_2Cl$ and $RCOCH_2Br$ obtained will be in proportion to the relative rates of reactions 14a and 14b.

$$RC(=O)^{-} = CH_2 + HOCl \rightarrow RCOCH_2Cl + OH^- \qquad (14a)$$

$$RC(=O)^{-} = CH_2 + HOBr \rightarrow RCOCH_2Br + OH^- \qquad (14b)$$

even though the overall rate is governed by reaction 13. Similar considerations apply to the later stages of the reaction sequence, for reactions 15 and 17, though faster than reaction 13, are slow compared with their succeeding reactions in each case.

Ethanol, acetaldehyde, methyl ketones and secondary alcohols with the general formula CH_3CHOHR are among the compounds or classes of compounds that give the haloform reaction. So also may unsaturated compounds with a structure $CH_3CH = CR_1R_2$, for, after addition of HOCl to give $CH_3CHOH\ CR_1R_2Cl$, oxidation will give a methyl ketone. Possible sources of haloforms are thus very extensive.

Organic Compounds in Water Supplies

Natural waters, even when unpolluted, may contain a great number of different organic materials. The extensive review of Vallentyne (161) described thousands of compounds of widely diverse types that have been found in natural waters, but, even so, only a small fraction of the total organic material present in a given natural water has been fully characterized. Most researchers have restricted themselves to detecting or determining the compounds belonging to a particular class of compounds.

The total organic matter dissolved or colloidally dispersed in typical unpolluted natural waters as determined by general methods for total organic carbon or COD seems to fall in the range from one to a few tens of milligrams per liter. Since analyses by carbon adsorption methods generally indicate only a few tenths of milligram per liter, it is apparent that these methods do not recover fully the organic materials in natural waters, although they may be very effective for certain obnoxious classes of compounds.

The major, almost the sole, source of organic matter in unpolluted water supplies is plant material, either synthetic units, metabolic intermediates, end products or decomposition residues of the biochemical activities of members of the plant kingdom ranging from bacteria and algae to forest trees. This unified source does not, however, place much restriction on the number or variety of individual chemical components that may be encountered. Not only the major structural and storage compounds with

their antecedent or breakdown products need be considered, but also the wide range of individual scents, flavors and other distinctive materials that characterize separate forms of plant life.

Among just the broad classes of chemical compounds that have been found to be present are: carbohydrates, proteins, lipids, nucleic acids, terpenoids, carotenoids, chlorophylls, vitamins, carboxylic acids, esters, amino acids, phenolic compounds, steroids and humic substances. (43, 161) In the following sections these and other classes of compounds are surveyed with regard to their presence and concentration in water supplies, but this can be done in only a general way because of lack of sufficient information.

A. Humic Substances. One of the most significant classes of compounds contributing organic matter to water is the humic material which causes the yellow to brown stain of surface waters. The humic substances arise principally by extraction of the soluble fraction of wood tissues, by dissolution or dispersion of decomposition products of decaying wood or leaves and by leaching of soluble components from soil organic matter. For the most part the material seems to have a molecular weight in the 10^4 - 10^5 range and to fall into the group of compounds designated as fulvic acids (12, 13,21). Different waters, as might be expected, exhibit different patterns of size distribution of molecular weights, according to gel chromatographic studies (54, 55,56). Chemically the humic material has been classified as aromatic polyhydroxymethoxycarboxylic acid.

Operators of water treatment plants have observed repeatedly that the chlorine demands of their upland surface supplies correlate closely

with the depth of color of the supply (21, 135) indicating that a large portion of the chlorine demand results from chemical reactions of hypochlorite with the humic substances. Except for the suggestions by Rook (124) however, there has been little investigation of the nature or the products of this interaction of hypochlorite with humic substances. The known elements of structure give many possibilities for reaction, some of which should yield the haloforms found by Rook.

B. Carboxylic Acids. Salts or esters of carboxylic acids comprise one of the major groups of small molecular weight organic compounds found in natural waters. Concentrations in the range of a milliequivalent per liter have been found (108, 110) corresponding to several milligrams per liter depending on the equivalent weight. Included in the total carboxylic acid group are simple aliphatic monocarboxylic acids, hydroxyacids and dicarboxylic acids associated with the Krebs' cycle and aromatic carboxylic acids such as benzoic and salicylic acids (109, 110).

The simple aliphatic monocarboxylic acids, except for formic acid, would not be expected to react with hypochlorite. Formic acid might be oxidized to CO_2 and H_2O. The hydroxylated acids, mono-, di- and tricarboxylic acids, are also subject to oxidation by hypochlorite, yielding keto acids and possibly chlorine substitution products depending on the structure. Decarboxylation and ultimate oxidation to CO_2 and H_2O are also to be expected in some instances. The concentrations of the hydroxylated acids should, however, be quite low, a few ppb. in most situations because they are such active substances as biochemical metabolites.

The aromatic carboxylic acids will react with hypochlorite in the

aromatic ring much as phenolic compounds do and should be otherwise non-reactive. Their possible effects will, accordingly, be discussed along with those of the phenols.

C. Sugars and Amino-Sugars. Many monosaccharides and oligosaccharides, especially glucose, xylose, ribose and their condensation products, should occur in natural waters because of their biochemical relationships. Little has been done, however, to determine their nature or concentrations (43, 161).

Simple reducing sugars are extensively oxidized by hypochlorite (83, 129) but there is no evidence that any chlorinated derivatives are produced. Ultimate potential oxidation to CO_2 and H_2O seems likely.

The amino sugars undergo N-chlorination like other amines and presumably undergo oxidative deamination subsequently.

D. Amino Acids, Peptides, Proteins. Free amino acids and related compounds have been found and partially characterized in some lake waters and the ocean (94, 48) but, on the whole, relatively little attention has been paid to these materials. The total amino-nitrogen content of unpolluted surface waters is usually several tenths of a milligram per liter, but whether this is primarily proteid, amino acid or other nitrogenous material is not known (43, 161).

Reactions of the amino acids with hypochlorite has been discussed previously in some detail. N-chlorination followed by oxidative deamination is the general pattern to be expected. With some structures decarboxylation and subsequent complete oxidation may result eventually with excess chlorine.

Reaction of HOCl with the peptide bond in peptides and proteins is much slower than its reaction with the free amino group. So, with excess free chlorine slow formation of N-chloropeptide bonds is expected. Such N-chlorinated derivatives of amides are in many instances quite stable and so available chlorine in these compounds may be very persistent. Formation of C-chlorinated derivatives is not known or expected generally.

E. Other Nitrogenous Compounds. In addition to the amino acids and proteins other important types of nitrogenous organic compounds are pyrrole and other porphyrin derivatives, formed in the breakdown of chlorophyll, and pyrimidines and purines, associated with the synthesis and breakdown of nucleic acids. No information is available on the occurrence of these types of materials in natural waters.

Jolley (83, 50) found, however, that a number of chlorinated pyrimidines and purines were formed during the chlorination of sewage effluent. Among these were 5-chlorouracil, 5-chlorouridine, 8-chlorocaffeine, 6-chloroguanine and 8-chloroxanthine. It is possible that additional substitution or oxidation may occur with the excess hypochlorite available in water chlorination rather than the chloramine prevalent in sewage chlorination.

F. Phenolic Compounds. Phenolic compounds occur in unpolluted water supplies as a result of the breakdown of lignins, tannins and other humic substances (66, 161). Decomposing oak and beech leaves are felt to be strong sources for aquatic phenolic materials. In addition to phenol itself, various cresols, dihydric phenols, hydroxybenzoic acids, guaiacol and other similar substances may be present. One study of river water

reported 37 different phenols, but many of these were of industrial rather than plant origin.

Reactions of hypochlorous acid with phenols have been described in detail earlier. The usual first reaction is a ring chlorination in the two or four position, followed by additional chlorination until all the ortho and para positions are occupied. Then the ring is split and full oxidation, eventually to CO_2 and H_2O, occurs (74, 91). Although no worker has as yet noted any remaining chlorine substituted products, it seems possible that some of the C-Cl linkages might be retained when the phenol ring is broken to end up as some sort of chlorinated derivative.

Other aromatic derivatives--hydroxyaldehydes, hydroxy benzoic acids and similar compounds--should react similarly. The same sorts of reactions should obtain with naphthols and other fused ring systems; also activated heterocyclic rings should behave similarly.

G. Terpenoids, Isoprenoids, Steroids, Carotenoids, Xanthophylls. Many organic compounds found in plants are derived from the carbon skeleton of isoprene. Among these are the terpenes and related alicyclic ring compounds, sterols and other steroidal materials, carotenoids, some vitamins, xanthophylls and numerous other coloring and flavoring materials. Most of these predominantly hydrocarbon-like materials, often with double bonds or ring structures, exist in simple molecular form within the plant cell or structure and are excreted into water when the plant dies or is damaged.

Little is known of the occurrence of these materials in natural waters or of their reactions with aqueous hypochlorous acid. However, the unsaturation and ring structures that are often present plus the fre-

quent key substitution of hydroxyl or other groups suggest that chlorination reactions with compounds in this class of materials may be quite significant and produce chlorinated derivatives of considerable importance. The structure of isoprene itself, $CH_2 = C(CH_3) - CH = CH_2$, for example, is such that it seems likely that chloroform or other chlorinated compounds might be produced during its oxidation.

Research is needed with this class of materials.

H. Other Classes of Compounds. There are many other types of compounds either known to occur or likely to be found in natural waters. Among these are mercaptans and other sulfur-containing compounds, phosphate esters, alkaloids, toxins and antibiotic substances. In general, the types of reactions previously described will hold for reactions of the hydrocarbon portions of these molecules and with oxidation or hydrolytic reactions occurring with the non- carbonaceous groups.

Usually, also, these components will be such a small portion of the total organic matter that their reactions will not make a major contribution to any chlorinated organic compounds that may form. On the other hand, the reaction pattern for a given class of organic compounds can be so modified by the presence of activating or stabilizing atoms or molecular groups that it is impossible to predict exactly when stable chlorinated derivatives may be formed. At some time, surveys of the reaction products formed when dilute aqueous solutions of abundant or significant members of each of these classes of materials are allowed to react with excess hypochlorous acid would be desirable.

I. Summary. Review of the likely chlorination reactions for the diverse

classes of organic compounds that may be found in unpolluted drinking water supplies indicates that three types of materials are prospective sources of stable chlorinated organic compounds. These are: (1) Substances capable of undergoing the haloform reaction; (2) Phenols and related aromatic compounds; (3) Pyrimidines and purines. For the second and probably the third class of compounds, ring rupture and oxidation to non-chlorinated products seems to occur before highly polychlorinated derivatives are formed. In contrast, the highly chlorinated chloroform or other haloforms are the end products of reaction with excess hypochlorite for the substances in class (1).

Reactions of porphyrins and other pyrrole derivatives and reactions of isoprenoid compounds need particular attention to see whether they are potential precursors of chlorinated organic products.

The Study of J. J. Rook

In July, 1974, J. J. Rook (124) reported the results of investigations on the drinking water supply for Rotterdam, Netherlands, in which he found that chloroform and other trihalogenated methanes were formed as a result of superchlorination of the water. Concentrations of total halogenated methanes ranged from somewhat more than 10 µg per 1. to about 100 µg per liter under differing conditions.

Additional experiments with unpolluted upland water and with extract of peat gave strong evidence that it was the natural coloring materials in the water that gave rise to the haloforms. Some idea of the yield can be obtained from the fact that the peaty extract which contained 5 to 8 mg. per liter of total organic carbon or about 5×10^{-4} atom per liter gave rise to 2.0 µmol per liter of mixed haloforms, a yield of 0.4%.

Rook's results are reliable and his conclusions are well-established and plausible. They must be accepted as valid and significant.

It is important to note also some negative aspects of Rook's work in an assessment of its overall significance. No chlorinated derivatives of hydrocarbons other than methane were found, implying that the formation of chlorinated derivatives is restricted to the haloform reaction, or at least that this is the major reaction path for the formation of chlorinated organic compounds in water. The conclusion is not quite as firm as it might be, for the headspace chromatographic method used detects only volatile compounds, but at least some of the chlorinated ethanes should have been detected if they had been produced in significant quantities.

Even the carbon tetrachloride that was detected and cannot be accounted for by the haloform reaction was found to be an impurity in the gaseous chlorine used.

Consequently, the only stable chlorinated compounds known to be produced by chlorination, apart from the odorous chlorophenols that are destroyed by free residual chlorination, are the halogenated methanes. Other chlorinated organic compounds, like those found in the New Orleans drinking water study, must have come from pollutional discharges and not from the chlorination of the water.

Moreover, although chlorination of the water was found to produce haloforms, it was also destroying detectable concentrations of organic pollutant, possibly toxic in nature. Rook made the comment, "Comparison of headspace fingerprints of water before and after breakpoint chlorination indicated that the volatile micropollutants passed this treatment step in diminished concentration." The volatile micropollutants had previously been stated to include freons, chlorinated solvents, lower alkanes and substituted benzenes and toluenes.

Rook also points out that the haloforms are significantly adsorbed by activated carbon and also are removed by volatilization during flow in open channels and by cascade aeration.

The Work of Bellar, Lichtenberg and Kroner

Later in 1974 the results of a study similar to that of Rook were published by Bellar, Lichtenberg and Kroner of the National Environmental Research Center of the EPA in Cincinnati (10). These authors found by headspace chromatography substantial concentrations of haloforms to be present in a variety of finished drinking waters from Ohio, Indiana and Alabama, in concentrations ranging from about 50 µg per liter to almost 200 µg per liter. Drinking waters from nearby well-water sources showed less than 10 µg per liter of haloforms.

Further investigation of one of the surface supplies showed that the raw water contained less than 1.0 µg per liter of haloform and that the haloform increased to more than 100 µg per liter after chlorination of the water. Unfortunately, the compounds responsible for the formation of the chloroform could not be identified, for the raw water was the Ohio River, which had been polluted extensively upstream with a wide variety of organic chemicals.

Bellar, Lichtenberg and Kroner showed that haloform formation was slow in their water, requiring up to 24 hours for full development with a single dose of free chlorine. This may be one reason for the greater concentrations of haloforms found in this study as compared with Rook's findings. Additionally, however, the concentrations of chlorine used were generally greater.

The work of Bellar, Lichtenberg and Kroner is less thorough and well-rounded that that of Rook. The one additional point it may add to

Rook's work is the indication that other substances than the coloring matter of water may produce haloforms. It accords with Rook in not finding chlorinated organic compounds other than the haloforms although the stripping procedure used was designed to detect compounds with boiling points up to 150°C.

Bellar, Lichtenberg and Kroner also attributed the production of the haloforms to the haloform reaction, but suggested that they came from ethyl alcohol, also detected in the water. They performed no follow-up experiments, however, to show whether or not ethyl alcohol produces chloroform when chlorinated under the conditions of water treatment.

Health Hazards in Water Chlorination

Considerable interest in problems associated with the presence of chlorinated organic compounds in drinking water was aroused in 1974 by the publication of studies purporting to relate the occurrence of such compounds with cancer rates in New Orleans (37, 162) and with the finding of volatile chlorinated organics in the blood of patients at a New Orleans hospital (31).

The evidence for a relation between cancer incidence and drinking water quality in New Orleans is far from conclusive. Even if this relationship were firm, there is no evidence to show that it is the chlorinated organic compounds in the drinking water that are responsible for the relationship. (Presumably this class of compounds has received particular notice because it includes chlorinated pesticides and vinyl chloride, and because chlorinated compounds are detected with high sensitivity by gas chromatography.) Beyond this there is no evidence that water chlorination is responsible for any of the chlorinated organic compounds found at New Orleans.

Apart from the chlorophenols, whose formation and subsequent destruction by aqueous hypochlorination are well documented, the only identified chlorinated products from the hypochlorination of water supplies are chloroform, bromoform and the mixed chlorobromoforms. There remains a possibility that non-volatile chlorinated organic compounds not detectable by the technique used are formed, but what meagre data there are on the products of the hypochlorination of natural organic compounds suggests that highly

chlorinated derivatives are not likely to form and that more moderately chlorinated ones are generally subject to oxidative decomposition by excess hypochlorite. The only waters in which an extensive variety of chlorinated organic compounds have been found have been those of rivers heavily polluted by discharges from chemical industries.

Accordingly, the finding of numerous chlorinated organic compounds in drinking waters derived from strongly polluted rivers is extraneous in one major sense to the question of health hazards induced by water chlorination. On the other hand, there is a good probability that when waters strongly polluted with chlorinated organic chemicals are subjected to free residual chlorination, a sufficient fraction of these compounds will be decomposed, as found by Rook, that the total concentration of chlorinated organic compounds is considerably reduced. Then, whatever toxicological or carcinogenic hazard is associated with the presence of chlorinated organic chemicals will be lessened rather than accentuated by hypochlorination. It seems possible that a partial solution to the problem of chlorinated organic compounds in New Orleans drinking water is an intensification rather than an abatement of hypochlorination. Obviously more complete chemical studies are required in addition to toxicological ones, so that a total balance of chlorinated organic substances and of other potentially hazardous materials as they are affected by hypochlorination of the water may be obtained.

With regard to the hypochlorination of otherwise unpolluted waters, the only known health problem to be addressed is the toxic or carcinogenic properties of the haloforms found to be produced in the hypochlorination

process. Since no information on the toxicities or carcinogenicities of bromodichloromethane, dibromochloromethane or bromoform could be found, the problem is reduced at present to a consideration of the toxic and carcinogenic properties of chloroform.

The acute toxic dose of chloroform to a number of test animals is given as about 1800 mg. per kg. (95). It falls in the same class of toxic substances as sesame oil and household sulfonated detergents in this respect (95). Chronic toxic affects seem to begin with daily doses in excess of 0.3 mg. per kg. body weight. At a dose rate of 0.4 mg. per kg. albino rats showed no effect, but guinea pigs exhibited increased vitamin C in the adrenals. At a dose rate of 12.5 mg. per kg. the albino rats showed disturbance of conditioned reflexes after four months(95).

With a chloroform concentration of 0.1 mg. per liter and a consumption of one liter per day, the intake rate of a 50 kg. individual would be .002 mg. per kg., about one two-hundredth of the minimum observed chronic toxicity level.

Robeck has noted that the allowed limits for industrial air exposure are about 1000 times as great as the expected water intake rate at the maximum concentration levels found.

With regard to the carcinogenicity of chloroform the International Agency for Cancer Research Monograph states that the carcinogenic potential of chloroform has been inadequately investigated so that as of 1970 it was not possible to extrapolate the carcinogenic risk of chloroform to man.

Three feeding studies, two of them to mice, have been reported in

the literature. In one of these, by Eschenbrenner and Miller (38, 39), liver hepatomas were observed, but only if the doses of chloroform were great enough to cause necrosis of the liver and death of a majority of the mice within 150 days. No hepatomas were observed with non-necrotizing doses of chloroform.

Rudali (127) in the second mouse study, administered 0.1 ml of 40% chloroform in oil twice a week. Three mice of 24 with an average life span of 297 days developed hepatomas; however, there was no untreated control group for comparison.

Hueper and Payne (72) fed rats 2% chloroform in their diets for 13 months; no hepatomas were observed in the 40 test animals.

There are also two studies in which chloroform was administered by subcutaneous injection, one with mice (123) and one with rabbits (80). Results of both studies were negative with respect to carcinogenesis of chloroform.

The conclusion must be that although substances of established carcinogenicity may be carried by polluted water supplies and distributed in drinking water, there is no evidence at present that the hypochlorination of water supplies makes the drinking water carcinogenic.

Recent Work of J. J. Rook

At a recent (Feb. 1975) meeting with Drs. Rook additional and more recent findings of his work were discussed. There have been no major new discoveries, but Drs. Rook was able to expand on some of the data and conclusions in his paper. A drinking water supply derived from the Meuse River and subsequently treated by a month or more of storage followed by slow-sand filtration was chlorinated at 0.5, 1.0, 2.0 and 5.0 ppm aqueous chlorine and subjected to head space analysis after an hour of contact. Haloforms in concentrations up to perhaps 50 micrograms per liter were found, in spite of the fact that biological activity during storage and slow sand filtration should have eliminated possible small molecule precursors like ethanol and acetone and in spite of the fact that the finished color was only 5 units. Apparently even high quality waters may contain biologically resistant natural organic matter, not as colored as the fulvic acids, that will produce haloforms upon chlorination.

Some model reactions that Rook has studied include the production of haloforms from alcohol and acetone. He has found that formation of chloroform from these substances at water pH values and milligram per liter concentrations is far too slow for these substances to be the source of the haloforms in water chlorination.

No very extensive studies have been made on the effect of pH. A few experiments were performed at the very low pH of 3.5 with some indication of reduced yields of haloform, but there was no dramatic change. There had been no studies of pH effects within the range 6 to 8.5 at the time

of meeting, but these were planned for the near future.

Data on the possible formation of other halogen derivatives than those of methane were scanty. Drs. Rook felt that some of his chromatographs showed chlorinated ethane, but he was not certain of its source and whether it was actually formed in the chlorination process. Larger chlorinated molecules were not generally detectable with Rook's headspace technique.

Rook had evaporated samples of some of his chlorinated waters and had obtained positive analyses for organically bound halogen on some of the residues in excess of amounts present in the unchlorinated waters. A large part of the organically bound halogen was bromine, giving additional indication of formation of these halogenated organic materials during water chlorination.

Rook had no indication of any formation of CCl_4 in the process of water chlorination.

In his earlier studies Rook had found that a number of compounds simulating portions of the proposed structures for humic substances, like pyrogallol and dihydroxybenzenes, react with dilute hypochlorite to give chloroform. More recent studies have not confirmed this; it now appears that reaction of these substances at the part per million level is too slow to account for the observed haloform formation.

One possibility is that <u>meta</u> rather than <u>para</u> or <u>ortho</u> dihydroxy substitution is needed to provide the required rate of hypochlorination. Since the haloform reaction depends eventually on a structure of the type $-\overset{OH}{C} = \overset{H}{C}-$, and this structure is found most readily in a compound like 1, 3,

5-trihydroxybenzene, it is perhaps to structures of this sort that one should look for precursors of the haloforms. Indeed, of the compounds investigated by Rook, resorcinol, m-dihydroxybenzene, seems to be the one exhibiting the required rate of reaction at the part per million level.

Possible Modifications in Treatment

The hygienic significance of the formation of haloforms during water chlorination is at present largely unknown. Health hazards claimed or foreseen for other chlorinated materials encountered as pollutants in natural waters should not be transferred willy-nilly to the haloforms.

Should any health hazard be shown to be associated with haloforms or other halogenated compounds formed in the process of water chlorination, then suitable modifications in source or treatment of the water should be sought to minimize or eliminate the occurrence of the hazardous materials without degrading the hygienic quality of the water in other ways.

The obvious step is to eliminate chlorination. Such a move would, however, mean a loss of all the benefits to health provided by chlorination: security from water-borne disease; maintenance of cleanliness and water quality in the distribution system; and simplicity and reliability in operation of the disinfection process. No other disinfecting agent, however powerful, provides all the advantages to health that chlorination does.

Moreover, no substitute disinfectant to chlorine should be recommended generally until it has been shown by studies as extensive and rigorous as those with chlorine that the use of such a disinfectant is more free from the production of noxious by-products than chlorination is.

If chlorination is to be retained, there are two approaches for minimizing the occurrence of noxious by-products in the finished water. One is to remove precursor material as much as possible before the water is

chlorinated. The second is to remove the chlorinated by-products after they have been formed.

The first approach means that prechlorination, which has been used widely as a general preconditioning step for water treatment, must be replaced by post chlorination after as much as possible of the organic material has been removed in other ways. Techniques of this type may be preferred when relatively unpolluted upland waters are being treated, for intensive chlorination of long duration is not needed for adequate disinfection with such waters. Preliminary treatment steps for reduction in concentration of precursor organic matter may be: (1) Storage for one to several months; (2) Coagulation-filtration; (3) Ozonation; (4) $KMnO_4$ treatment; or any combination of these.

The experience of Rook indicates that storage and coagulation, although useful in reducing the concentrations of haloforms, cannot be expected to eliminate them fully. Ozone is known to react only selectively with organic material in water, but its effectiveness on humic substances and its known reactivity towards double bonds may mean a very substantial reduction in haloform precursors. Permanganate provides a more general oxidizing action than ozone, but a less rapid and intense one. A combination of ozonation with some permanganate treatment may provide the most substantial overall reduction in organic matter.

The other approach, removal of haloforms and other formed chlorinated compounds following their formation, appears preferable when the source is a polluted one probably containing a substantial concentration of chlorinated organic material before any treatment. Best treatment of such waters

requires that some effort be made to remove the chlorinated substances already present in the raw water and this treatment may then also be utilized to take out haloforms produced during chlorination.

The most effective final treatment for removing chlorinated substances is, in all probability, adsorption on activated carbon. Aeration techniques can be used substantially to reduce haloform concentrations but is ineffective for heavier, less volatile molecules. Rook has found that powdered activated carbon has a good adsorptive affinity for haloforms.

When final adsorptive treatment is used for the removal of chlorinated substances, the initial prechlorination step should be intense, with maintenance of substantial residual free chlorine. There are two reasons for this recommendation. First, the presence of excess free chlorine will encourage the completion of the haloform reaction, yielding the relatively innocuous haloforms themselves, rather than partially chlorinated intermediates that may be both more hazardous and more difficult to remove. Second, the strong oxidizing potential of residual free chlorine seems to be effective in reducing the concentrations of some chlorinated organic substances present in typical polluted waters by oxidizing them to carbon dioxide and water.

Indicated Research Needs

Until the recent paper by J. J. Rook, the problem of the formation of chlorinated organic compounds during water chlorination had been almost completely ignored except for the reactions with phenolic materials. As a result the need for knowledge to be obtained from research is great and varied. Almost any accurate information related to the subject will be useful at least in providing orientation.

There are, however, certain subjects for research that seem most likely to provide an early assessment of the seriousness of the problem posed by the formation of haloforms and possibly other chlorinated organic substances during water chlorination.

A first priority should probably be determination of the extent of formation of other chlorinated materials than the haloforms. This will require somewhat more sophisticated techniques than simple head-space analysis, but might usefully be accomplished with some sort of initial low-pressure vapor-distillation concentrating process like that used by Silvey in obtaining odorous concentrates from actinomycetes. If no other significant compounds than the haloforms are found, the overall problem cannot be considered at present a very serious one.

A second issue that it would be well to have clarified as soon as possible is the yield of haloforms in relation to other parameters measuring aspects of organic matter in water, such as T.O.C., color, C.O.D. or permanganate value, CCE or CAE, etc. Only when some sort of correlation with properties such as these is shown will it be possible to

know what to aim for in the pretreatment of water to make it suitable for chlorination.

Third, the effects of diverse pretreatment steps should be studied with regard to the production of haloforms or other chlorinated organic substances. Obviously, such information is needed to assess the efficacy and benefit of possible pretreatment processes.

There needs also to be a study or series of studies, more fundamental in nature, to determine the dynamics and mechanism of the formation of the haloforms or other chlorinated organic substances. It seems clear that the pertinent reactions, at least in dilute aqueous media at the part per million level, are relatively specialized ones and do not indicate a generalized, random chlorine substitution. Also, the work of Bellar, Lichtenburg and Kroner indicates that the haloform-producing reactions are slow, and thus an understanding of the time dependence is important. Perhaps a dechlorination after fifteen to thirty minutes of disinfection would minimize formation of chlorinated derivatives. At the same time there should be dynamic comparison of the exertion of chlorine demand and the formation of haloforms. The relation between these will indicate the role of intermediates in the overall process.

Finally, because the standard haloform reaction is a classic example of a base-catalyzed organic reaction, there should be a detailed investigation of effects of pH on both the stoichiometry and the dynamics of formation of haloforms during water chlorination. This will serve not only as a clue to understanding the chlorination process, but also as a guide to best practice in minimizing extraneous chlorination.

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